High Energy Lithium Batteries for PHEV Applications

Subramanian Venkatachalam

Envia Systems

Project ID: ES211

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Program Overview

Time line

Start Date: Oct. 2013
End Date: Sept. 2015
Status: 25% Completed

Budget

Total Project Funding
$3.79 M
DOE: 80%
Cost Share: 20%

Barriers

- Meeting PHEV power specifications
- Loss of power with cycling
- Cycle and Calendar life

Partners

- Lawrence Berkeley National Laboratory (LBNL)

- General Motors (GM)

- Oak Ridge National Laboratory (ORNL)

Project Lead – Envia Systems

Project Objectives - Relevance

Goals

Develop a high capacity cathode, Si-C based anode and integrate them and build high capacity (0.25-40Ah) pouch cells that exceed the ABR minimum target goals for PHEVs

Relevance

- High DC-Resistance from HCMR™ Li-rich cathodes reduce the power and usable energy of the cell
- Growth in DC-Resistance with cycling reduce the life of the cell

Project Tasks

- Material development
- Nanocoating engineering
- Atomistic and cell-level modeling
- Material scale-up
- Large cell development
- Large cell testing

Cell Targets

Characteristics	Unit	PHEV40
Specific Discharge Pulse Power	W/kg	800
Discharge Pulse Power Density	W/L	1600
Specific Regen Pulse Power	W/kg	430
Regen Pulse Power Density	W/L	860
Recharge Rate	NA	C/3
Specific Energy	Wh/kg	200
Energy Density	Wh/L	400
Calendar Life	Years	10+
Cycle Life (at 30° C with C/3 Charge and 1C Discharge rates)	Cycles	5000
Operating Temperature Range	°C	-30 to +52

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HCMR^{TM} Cathode Layered-Layered Structure

Li_2MnO_3

$LiMO_2$
(M = Ni, Co, Mn)

x **Li_2MnO_3**• (1-x) **$LiMO_2$**
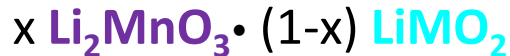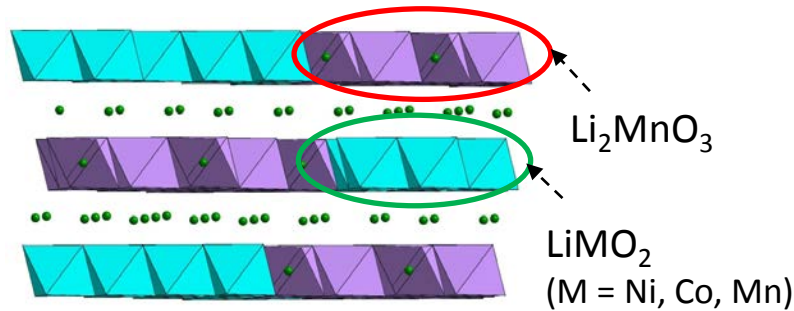
Envia has licensed Lithium-rich Layered-Layered Li_2MnO_3 · $LiMO_2$ composite patents from Argonne National Laboratory

Envia has developed HCMR™ (**H**igh **C**apacity **M**anganese **R**ich) cathodes based on layered-layered composite structures

Key benefits:

- High Capacity
- Low Cost
- High safety

Key issues:

- High DC-Resistance
- Voltage fade upon cycling
- Poor durability

During the First Charge:

(1) $LiMO_2 \rightarrow Li_{1-x}MO_2 + xLi^+ + xe^-$ where M = Ni, Co oxidation occurs ~ 3.7 V   *(Classical reaction)*

(2) $Li_2MnO_3 \rightarrow MnO_2 + 2Li^+ + 2e^- + 1/2O_2$ which is irreversible and is limited only to 1st charge   *(Typical of HCMR^{TM})*

During the Discharge:

(3) $Li_{1-x}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$

(4) $Li^+ + MnO_2 + e^- \rightarrow LiMnO_2$ (Li insertion into MnO_2)

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4

HCMR™ Cathode: Development Status

HEV, PHEV & EVs have different battery requirements ranging from power characteristics to cycle life. Envia solves the problem at the materials level by tailoring the cathode for each application.
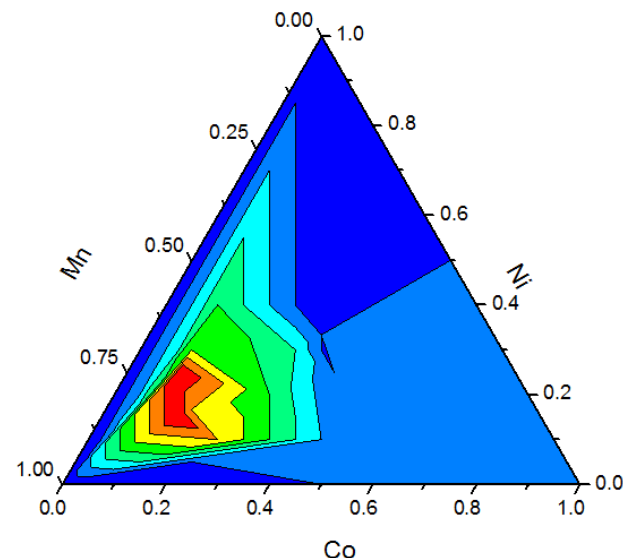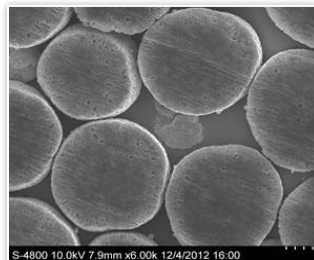
Morphology:

- Particle size, shape, distribution, tap density & porosity

Composition:

- Ni, Co, Mn ratio, & Li_2MnO_3 content
- Dopants concentration

Nanocoating:

- Chemistry: fluorine, oxide, etc.
- Thickness & uniformity

S-4800 10.0kV 7.9mm x6.00k 12/4/2012 16:00

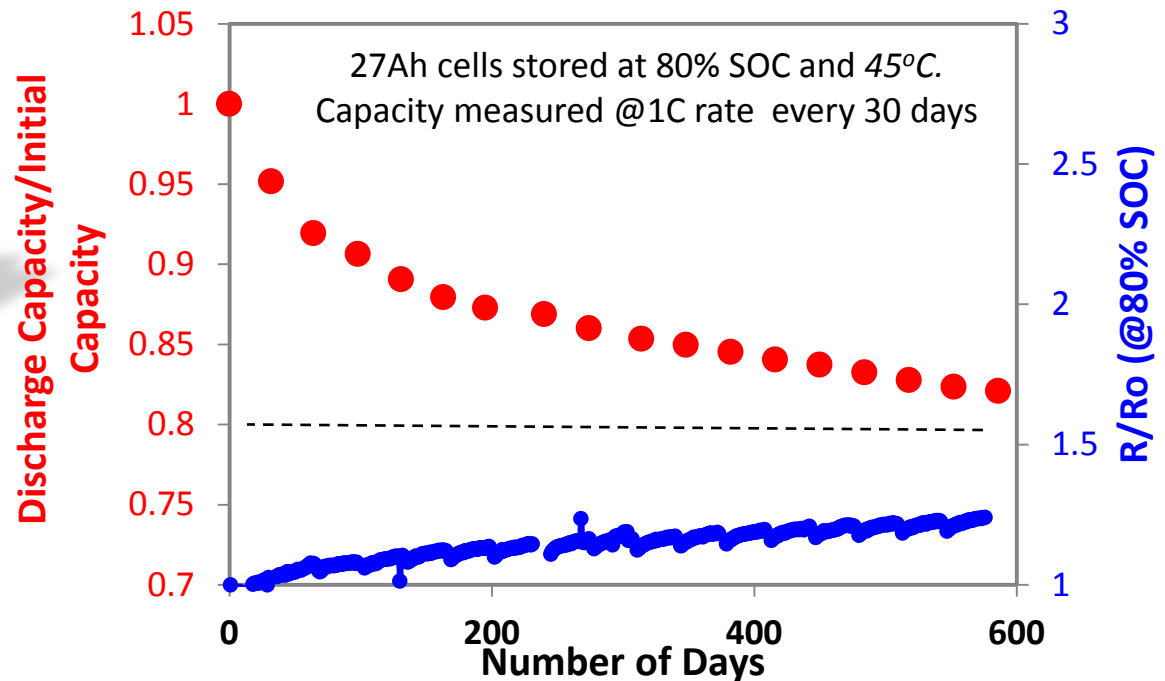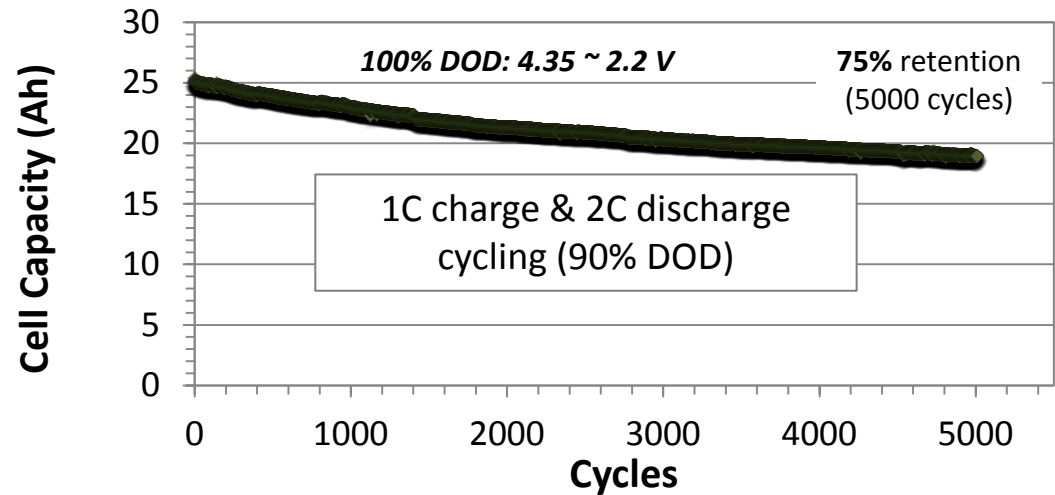| HCMR™ Type	C/10 Capacity Range mAh/g (4.6V-2.0V)	Status
XP	200 ~ 220	Commercialization
XE	225 ~ 240	R & D
XLE	240 ~ 280	R&D

- In the ABR program, Envia is currently using HCMR™ – XLE cathode
- Detailed cathode specifications are shared with the partners

PHEV Cell with HCMR^{TM} XP Cathode
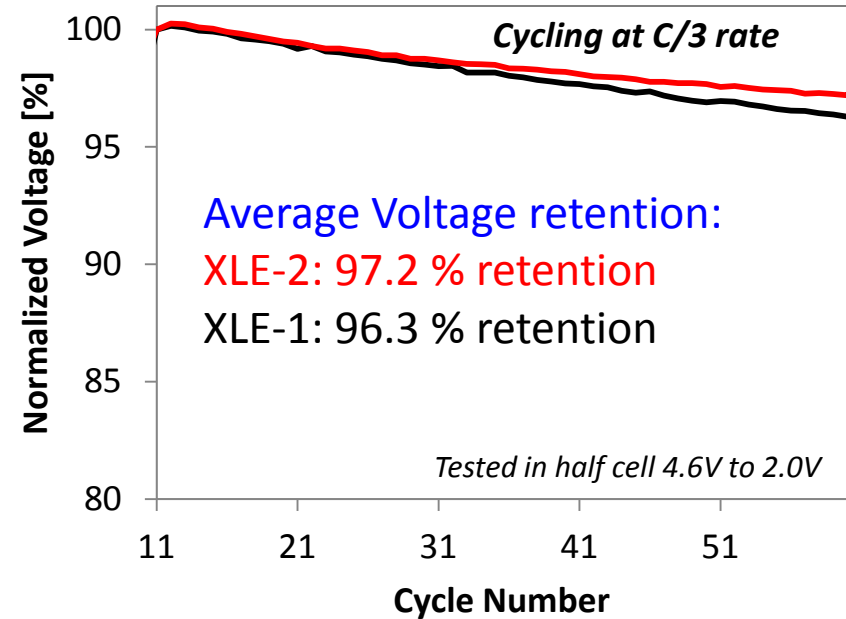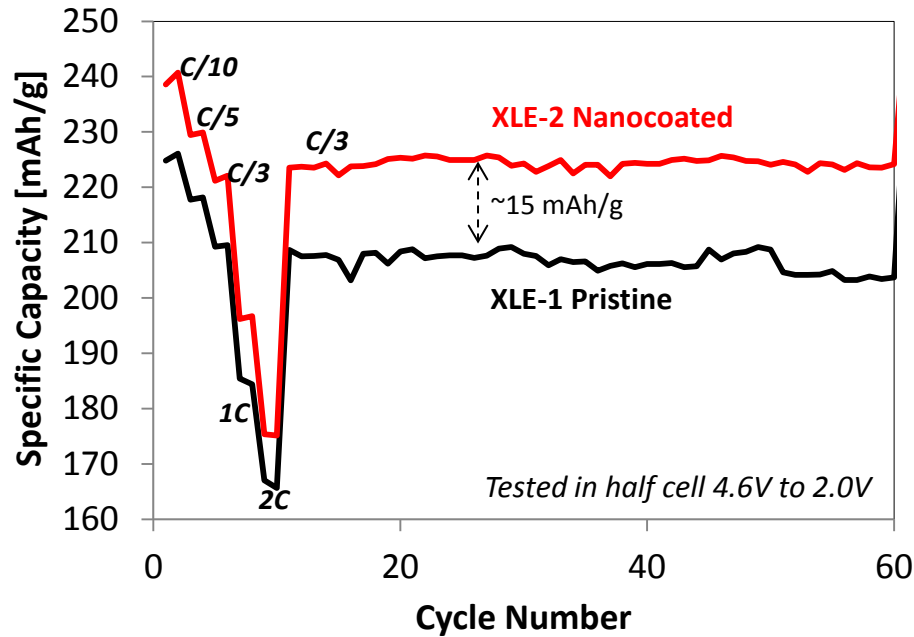
**107 Wh, 27 Ah Cell
180 Wh/Kg at 1C
with graphite anode**

HCMR™ XP cells
show **no** Voltage Fade

100% DOD: 4.35 ~ 2.2 V   **75%** retention
(5000 cycles)

1C charge & 2C discharge
cycling (90% DOD)

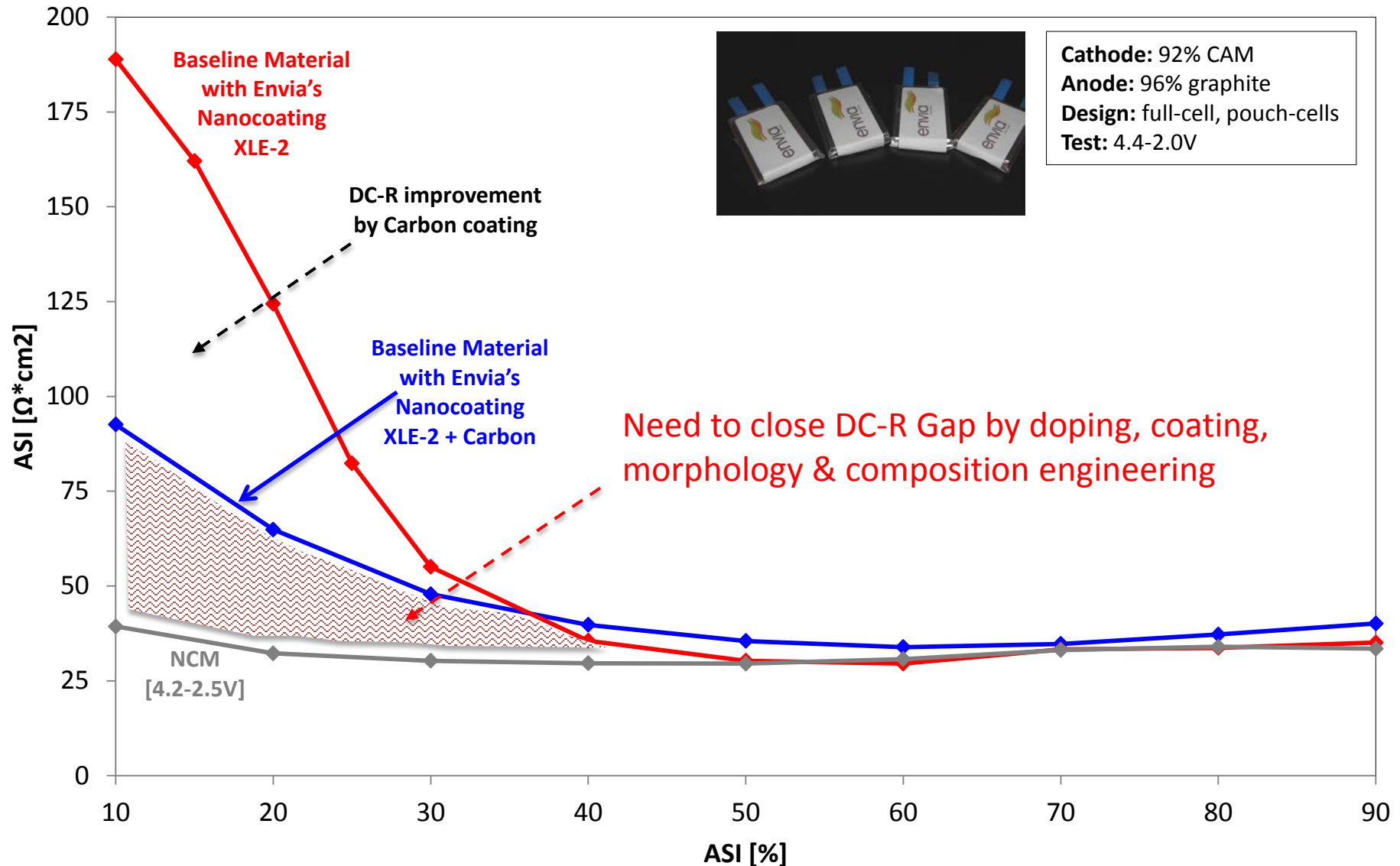27Ah cells stored at 80% SOC and *45°C*.
Capacity measured @1C rate every 30 days

HCMR™ XLE Cathode – Electrochemical Chemical Performance

- Baseline HCMR™ cathodes shipped to all program partners

- Nano-coating increases specific capacity (~15mAh/g) showing good capacity retention after 50 cycles at C/3

- Pristine material shows ~30mV higher voltage than the nanocoated material at the 1st C/3 cycle, however, at the 50th cycles both materials show similar average voltage

- Nanocoted cathode has lower voltage fade about 2.8% in a half cell. In a full cell the average voltage stabilizes to 2-3% fade after 150 cycles

DC-R Improvement by Carbon Coating

Baseline Material with Envia's Nanocoating XLE-2

DC-R improvement by Carbon coating

Baseline Material with Envia's Nanocoating XLE-2 + Carbon

Need to close DC-R Gap by doping, coating, morphology & composition engineering

NCM [4.2-2.5V]

Cathode: 92% CAM
Anode: 96% graphite
Design: full-cell, pouch-cells
Test: 4.4-2.0V

ASI [Ω*cm2] (y-axis)

ASI [%] (x-axis)

DC-R Impact on Usable Energy and Power

Amount of Li_2MnO_3 in HCMR™ cathode materials determine the usable power and energy of the cell

An increase in DC-R translates to a significant loss of power

Discharge DC-R test:
10 sec, 1C discharge pulse from single-layer pouch-cells
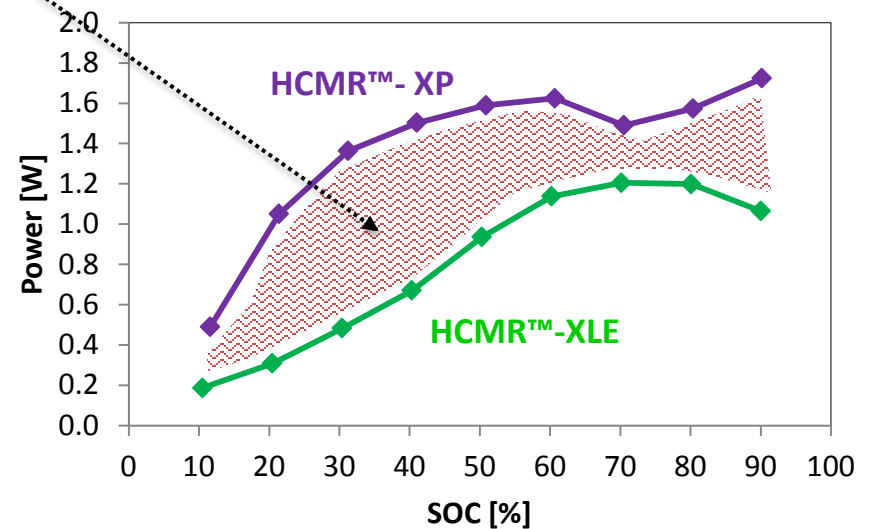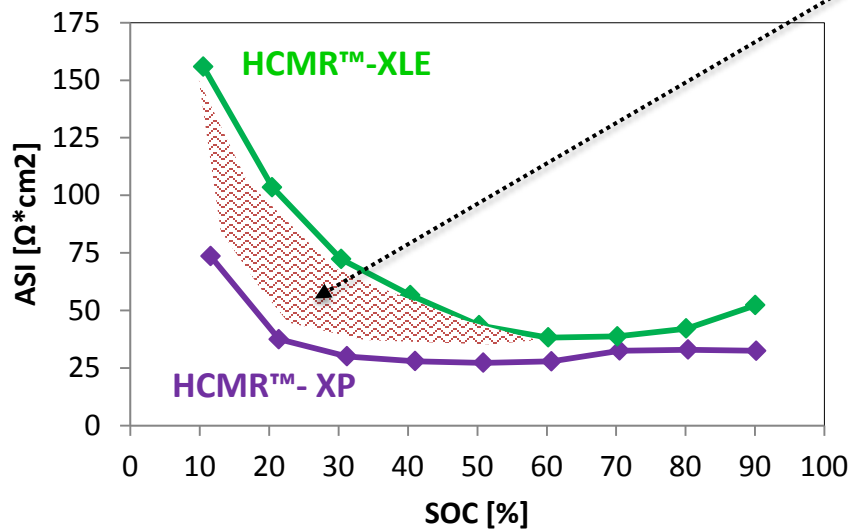
- HCMR™ XLE cathodes show a sharp increase in DC-R starting at 50% SOC which translates to a significant drop in power and lower usable energy

- On the contrary, HCMR™ XP cathodes show a flat DC-R profile from 90% to ~20% SOC translating to higher power and greater usable energy

DC-R– Models and Approaches for Improvement

Root cause	Development Areas	Team

Ionic conductivity
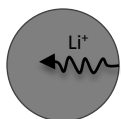
- Composition engineering of Li_2MnO_3 — Envia
- Dopant engineering — Envia/LBNL
- Reduction of particle size (morphology engineering) — Envia
- Reduction of O_2 defects during formation — LBNL/Envia

Electronic conductivity
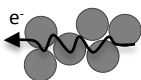
- Carbon coatings — Envia/GM
- Dopant engineering — Envia/LBNL
- Conducting polymer coatings — LBNL

Charge transfer resistance
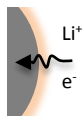
- LiPON nanocoating optimization (ionic) — ORNL
- Nanocoating optimization (electronic) — LBNL/GM/Envia

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10

Project Development Roadmap
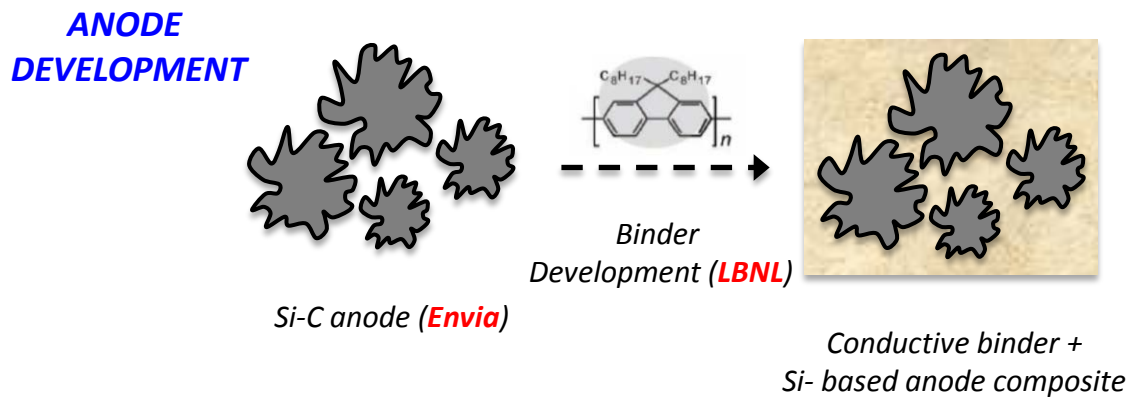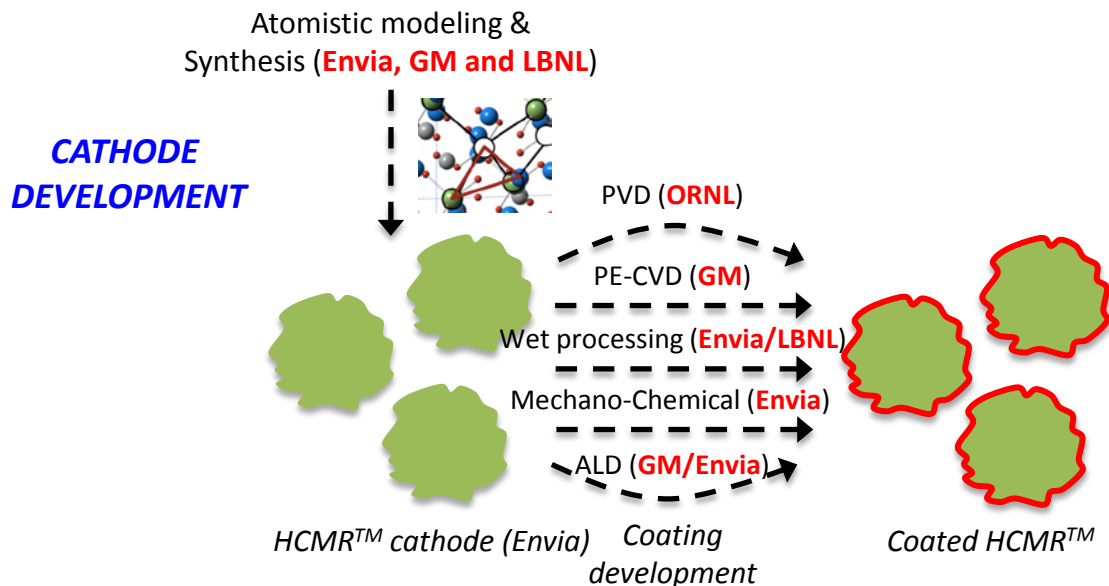
CATHODE DEVELOPMENT

Atomistic modeling & Synthesis (**Envia, GM and LBNL**)

PVD (**ORNL**)

PE-CVD (**GM**)

Wet processing (**Envia/LBNL**)

Mechano-Chemical (**Envia**)

ALD (**GM/Envia**)

HCMR^{TM} cathode (Envia)   *Coating development*   *Coated HCMR^{TM}*

ANODE DEVELOPMENT

Si-C anode (Envia)

Binder Development (LBNL)

Conductive binder + Si- based anode composite

CELL INTEGRATION (Envia) & TESTING (All)

High capacity cells to meet PHEV ABR cell targets

11

Nanocoating LiPON via Physical Vapor Deposition

Sputter Gun — Li$_3$PO$_4$ Target

Atomic Flux — N$_2$ plasma

Li$_{3.2}$PO$_{2.8}$N$_{0.2}$

Rotating cup filled with electrode

LiPON

- Stable to 5.5V
- Stable against Li
- Stable in liquid electrolyte
- Grown by vapor deposition in N$_2$ plasma
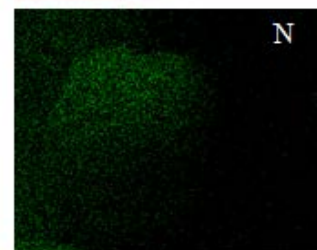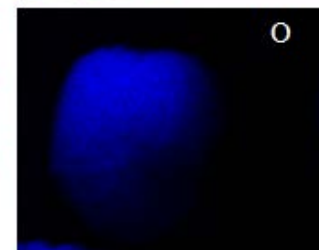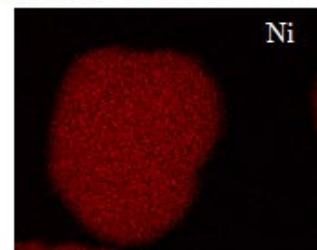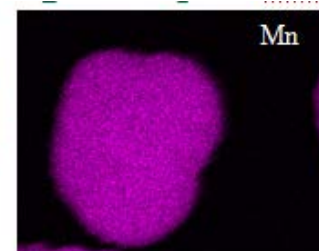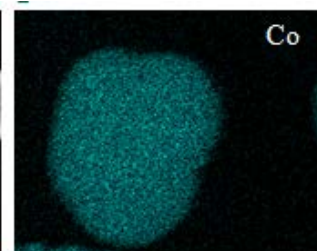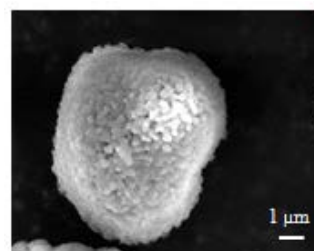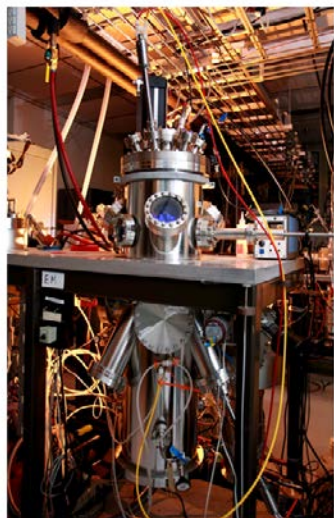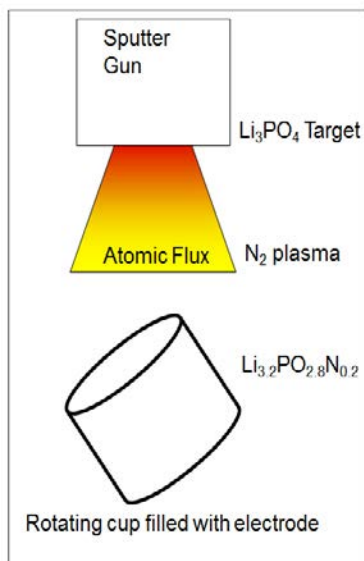
1. Secondary cathode particle aggregates appear to have similar morphology as uncoated or pristine cathode.

2. Shows nitrogen and phosphorus signal indicating homogenous coating

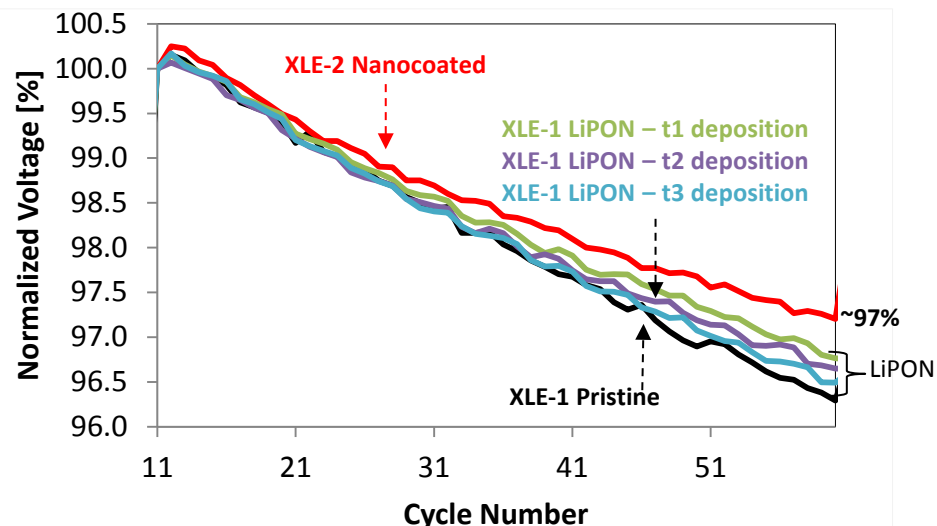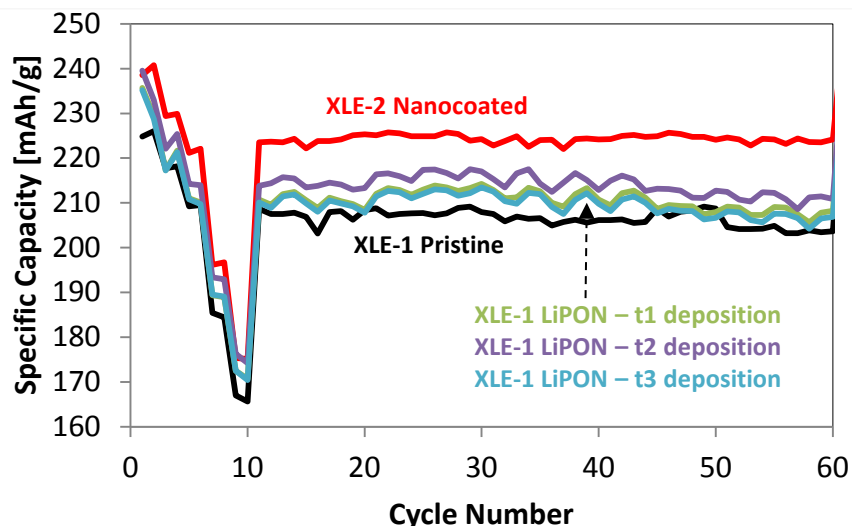3. No attrition or degradation from grinding powders during deposition

P content from Lipon goes up with increasing deposition time

Based ICP data

at% P vs Deposition Time (h)

XPS — N1s data

24 H
7 H
1 H

Binding Energy (eV)

Increase in N content with deposition time

Source: ORNL

LiPON Coated HCMR™ Materials

- LiPON-coated cathodes show ~50mV higher average voltage than uncoated cathodes after 50 cycles at C/3

- LiPON-coated materials show ~5-10mAh/g higher capacity than uncoated cathodes

- Voltage retention is improved from ~96% (uncoated) to ~97% (LiPON-coated) by LiPON deposition, specially for low deposition times

- Optimal LiPON thickness will be applied to the HCMR™-XLE2 to improve DC-R and high voltage durability (cycle life and calendar life)

Tested in half cell 4.6V to 2.0V

Nanocoating of HCMR™ Materials via ALD Process

Objectives: *(1) Explore different ALD nanocoatings - Al_2O_3, AlF_3, AlN, ZnO, TiN etc. (2) Optimize the best ALD conditions to get uniform nanocoatings without compromising capacity (3) Investigate the effects of ALD-coated materials on the DC-R of HCMR^{TM} cathode materials*

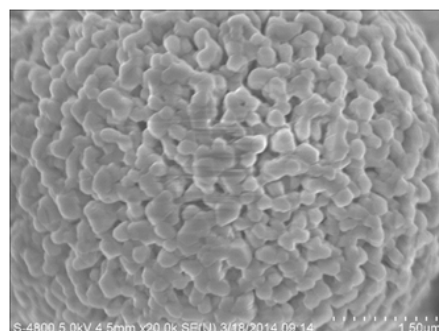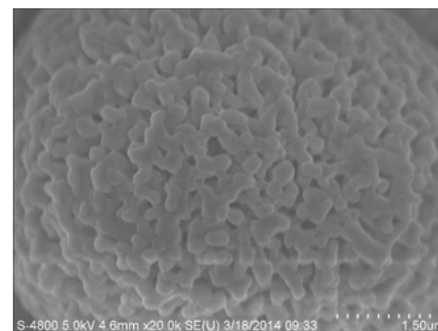$$2Al\,(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4$$

$$Al\,(CH3)_{3\,(g)} + :Al\text{-}O\text{-}H_{(s)} \rightarrow :Al\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$$

$$2\,H_2O_{(g)} + :O\text{-}Al(CH_3)_{2\,(s)} \rightarrow :Al\text{-}O\text{-}Al(OH)_{2\,(s)} + 2\,CH_4$$

- Self-limiting sequential surface chemical reaction;
- Conformal coating on 3D structure;
- Precisely control the thickness (1 cycle ~ 1.1 Å thick)
- Low temperature deposition;

100 nm

Al   Co

F   Mn

AlF_3 coatings with a thickness ~10nm are uniformly deposited on the surface of the HCMR^{TM} particles
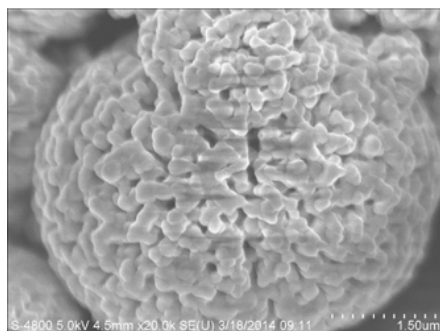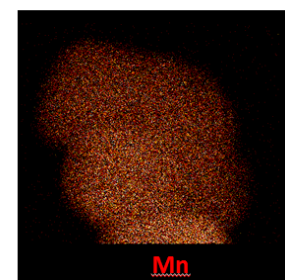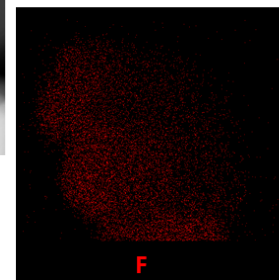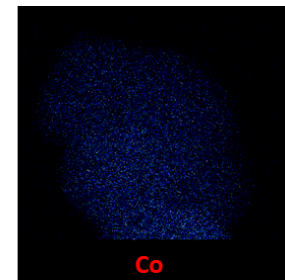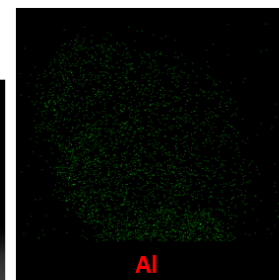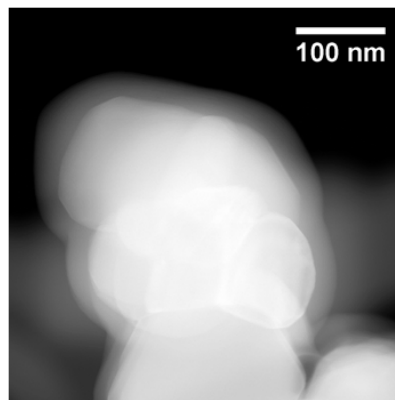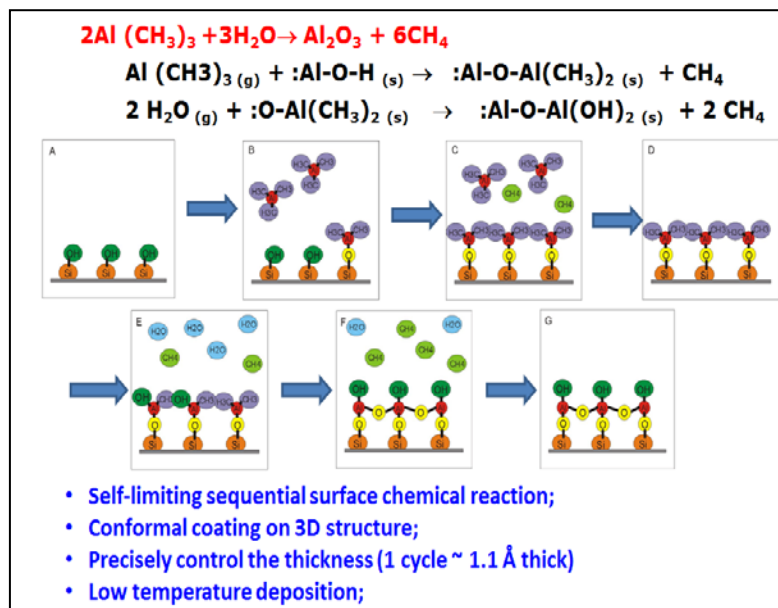
Pristine powder AlF_3 coated Al_2O_3 coated

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Source: GM

ALD Coated HCMR^{TM} Materials
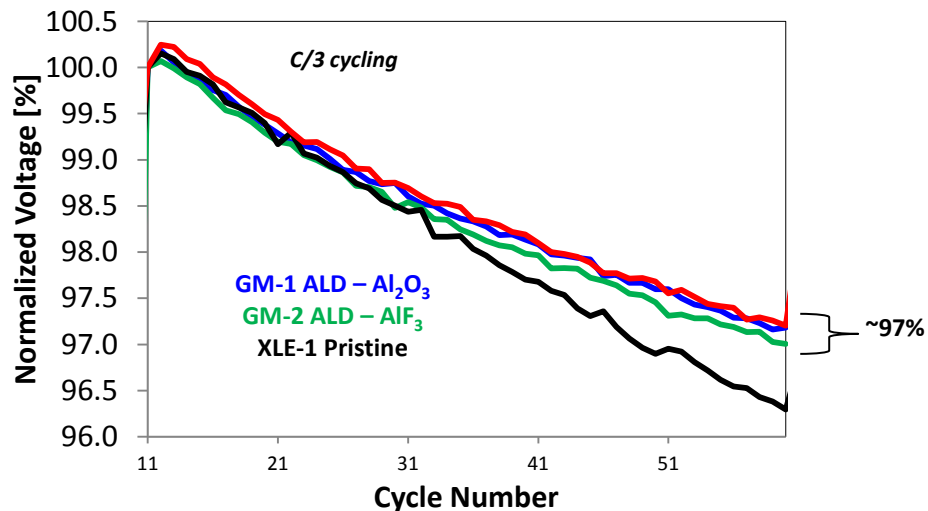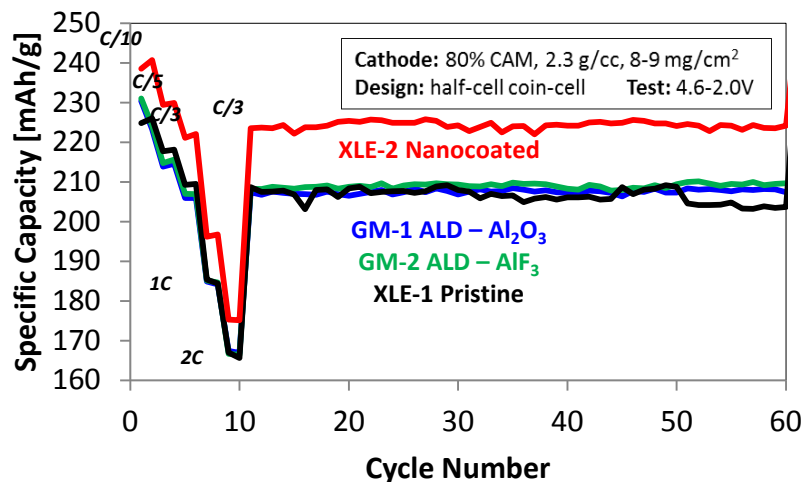
- ALD coated cathodes show capacities similar to pristine cathodes

- ALD coated cathodes improve capacity retention, absolute average voltage and average voltage retention (~1%) when compared to the pristine cathodes

- Optimized ALD nanocoating will be applied to the HCMR™- XLE2 (Envia nanocoated) to improve DC-R and high voltage durability (cycle life and calendar life)

Tested in half cell 4.6V to 2.0V

Material Challenges and Diagnostic Tools

Material Challenges

- DC-R
- DC-R growth with cycling
- Capacity fade
- Possible side reactions
- Possible structural transformation

Full suite of tools

- EIS (Deeper insight in DC-R)
- HPPC (Standard test of DC-R)
- SEM/TEM (Morphology changes)
- EDX (Elemental analysis)
- XRD (Bulk structural changes)
- FT-IR (Chemical bonding changes)
- Raman (Chemical bonding changes)
- Model system (Carbon and binder free)
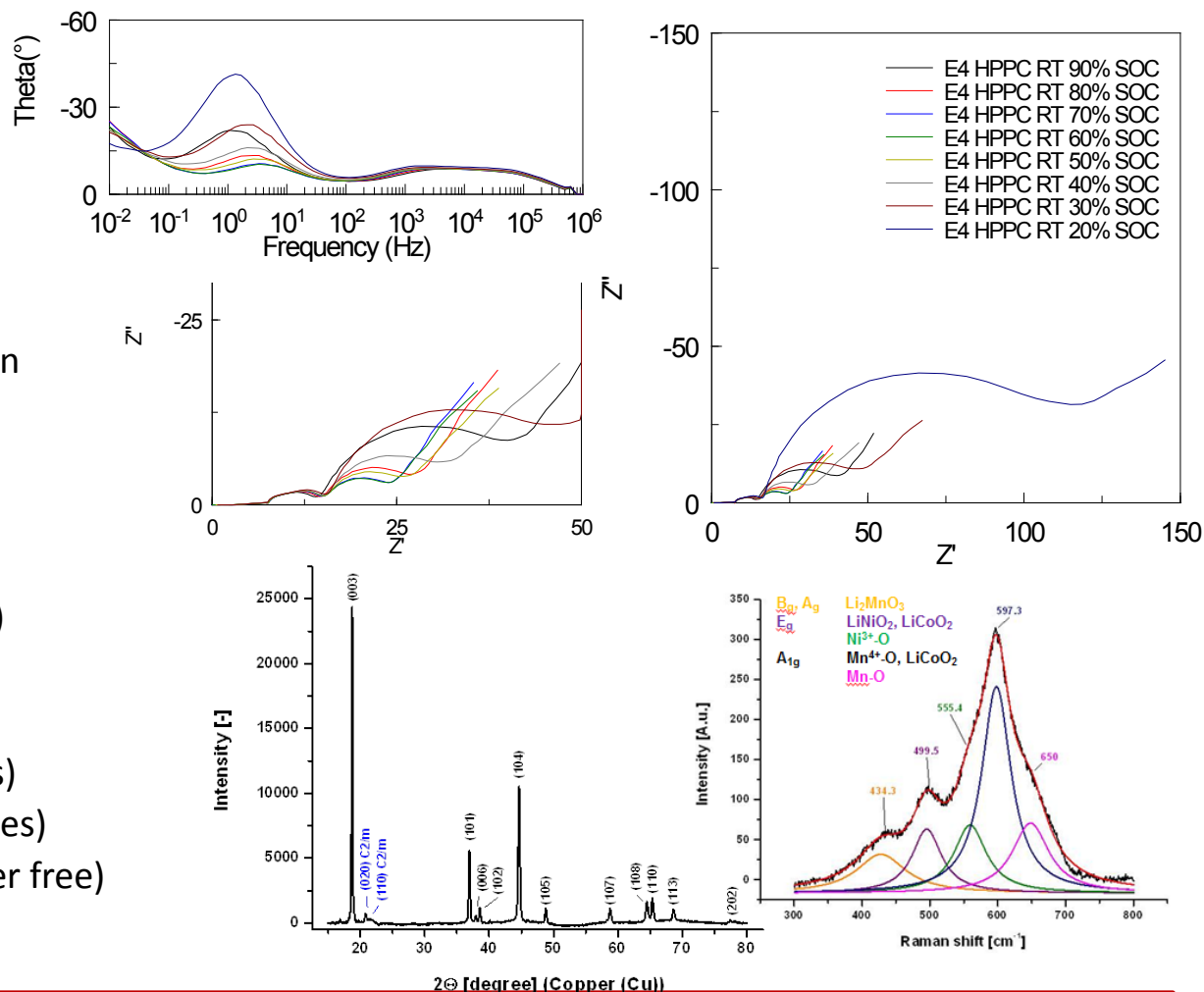
Goal: Correlate electrochemical changes to their physical location in the cell to determine cause of these phenomena
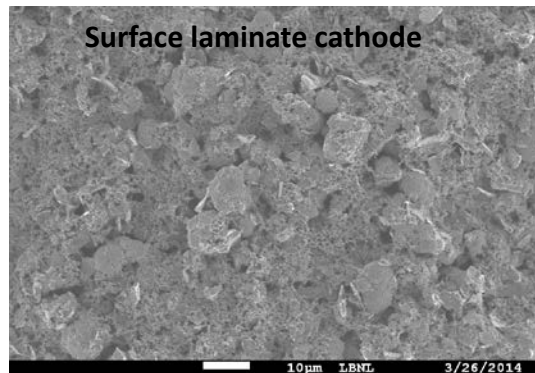
Source: LBNL

Characterization Approach

Laminate Cathode Electrode

- Cathode powder is laminated & calendared with additives (binder and carbons) into an Al current collector
- Testing in coin cell setup

Advantages:

- Approach reflects actual cell application
- Testing matches DOE standards
  → HPPC Testing

Surface laminate cathode
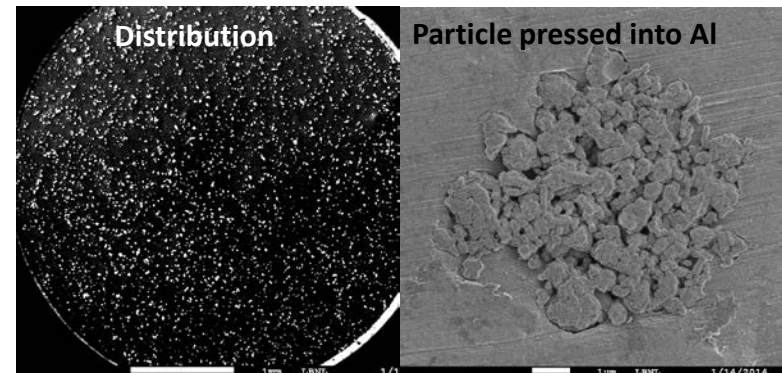
Carbon and Binder Free Electrode

- Pressing pure 100% cathode powder on Al foil
- Ideal (Model) system
- Testing in coin cell setup

Advantages:

- Signal is only from active cathode material
- Easier for characterizing degradation mechanisms

Distribution   Particle pressed into Al
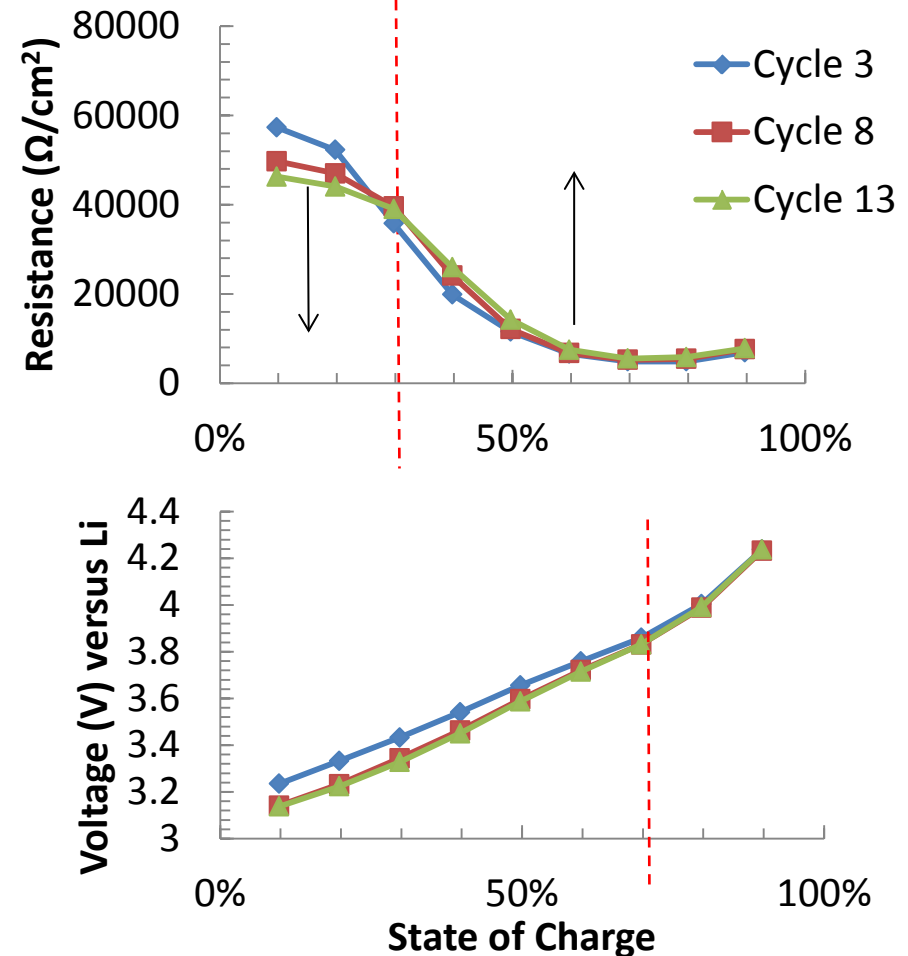
Source: LBNL

HPPC – Laminate vs. Binder/Carbon Free Electrode

Laminate Cathode Electrode
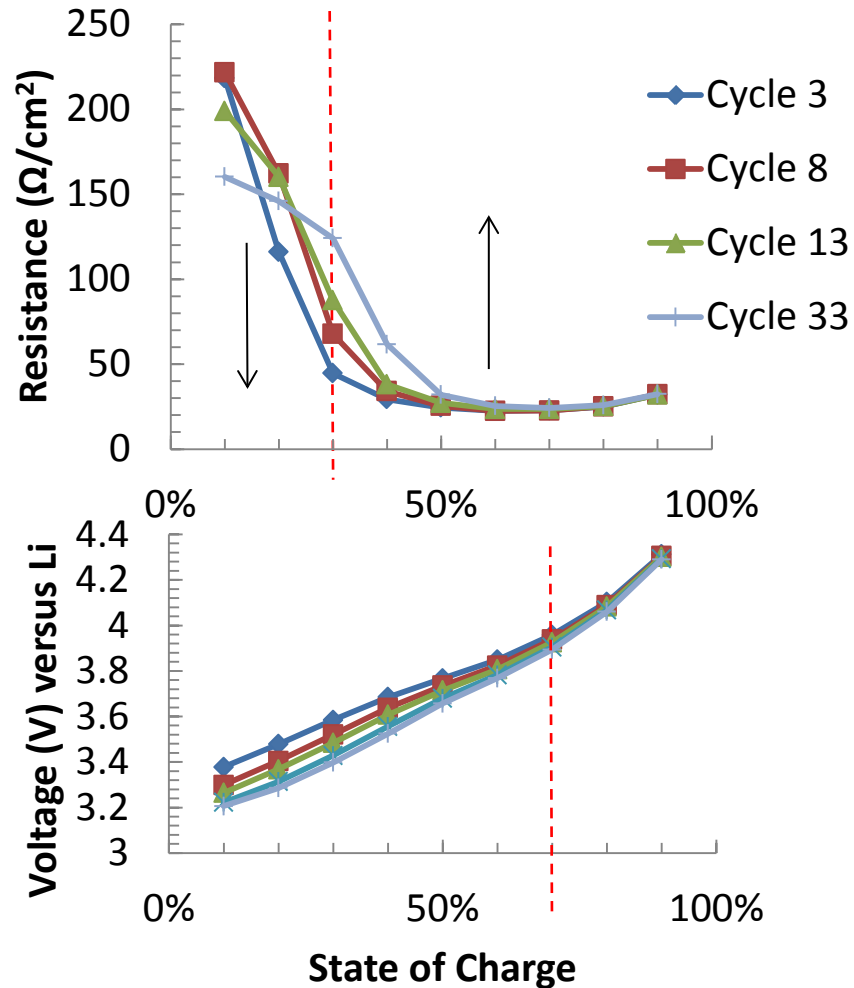
Carbon and Binder Free Electrode

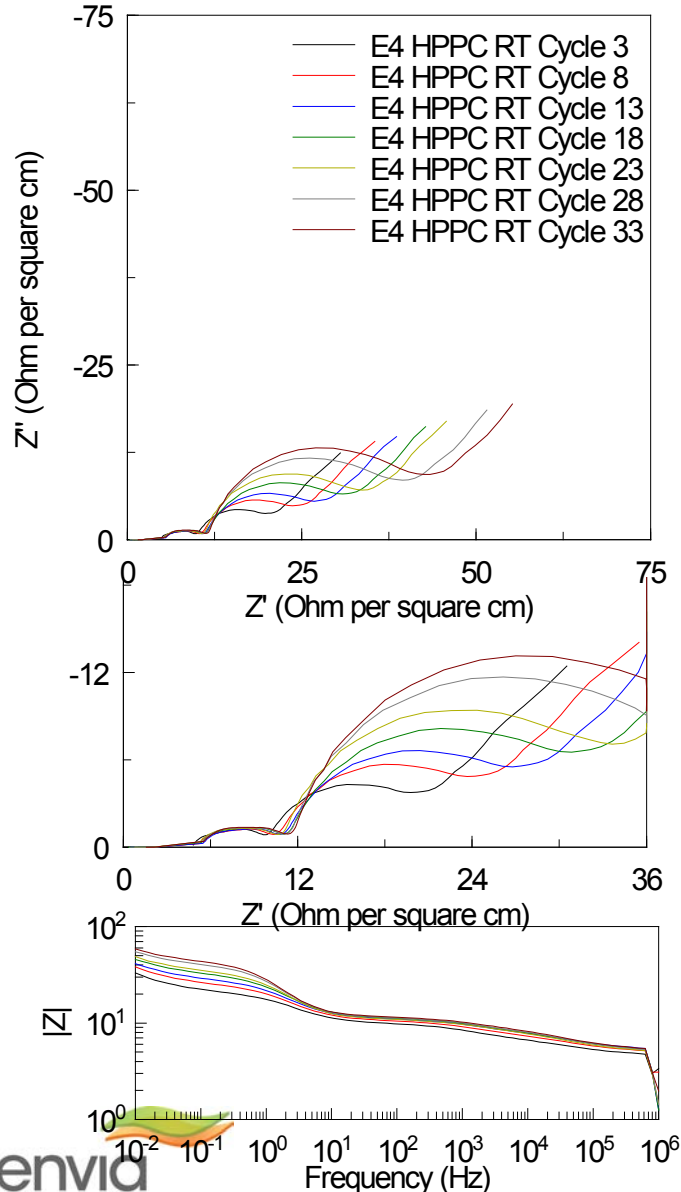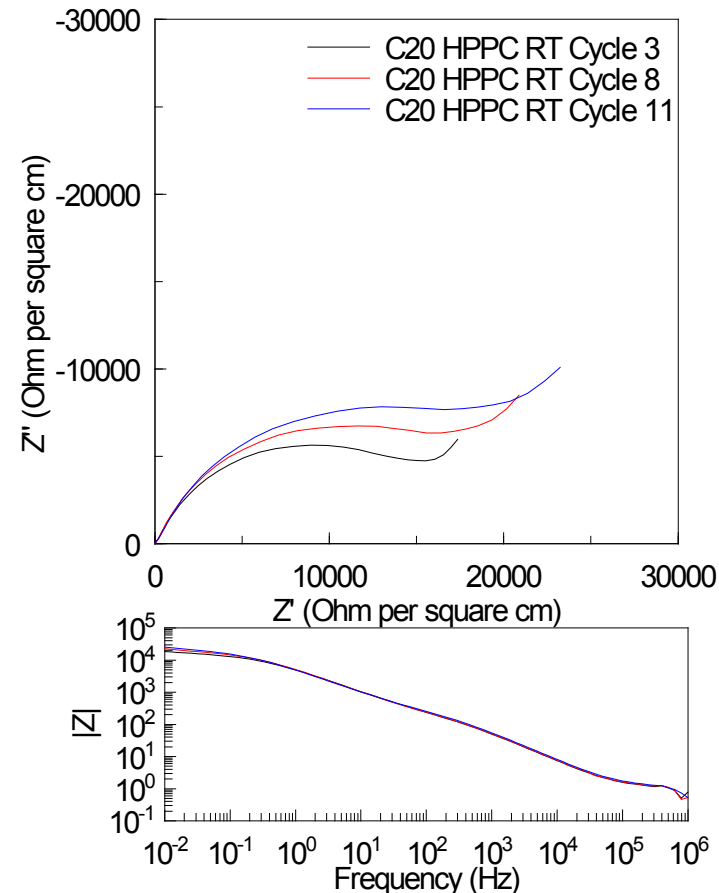*Source: LBNL*

- DC-R **drops** with cycling < 30% SOC
- DC-R **rises** with cycling 30% to 90% SOC
- Voltage Fade < 70% SOC

Impedance for Insight into DC-R at 40% SOC

## Laminate Cathode Electrode

Carbon and Binder Free Electrode

Source: LBNL

- Cycling increases low frequency semicircle
- DC-R growth because of slow time constant process (Slower than typical charge transfer process)

Theoretical Modeling – DC-R and Phase Change

✓ Stable intermediate states as a function of SOC (while keeping the layered structure) were predicted

x=0   x=0.5   x=1   x=2

← charging
→ Discharging
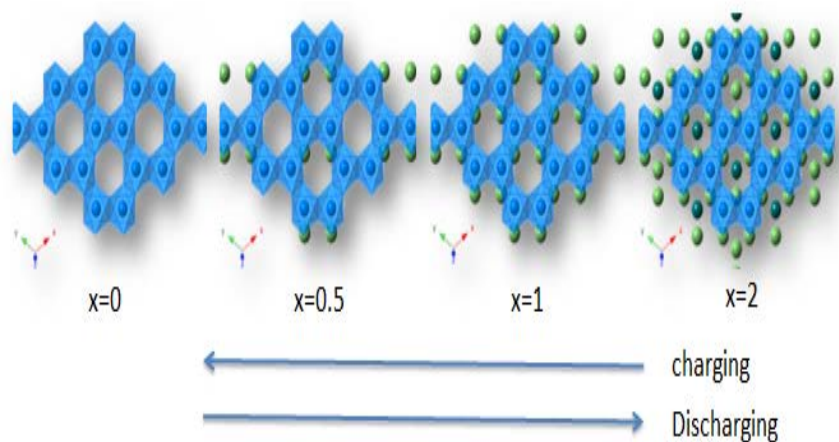
❑ **At each stable intermediate state,**

- Energy barrier calculation for Li hopping to a nearby site: Li ionic conductivity
- Density of states calculation to get the band gap: Electronic conductivity

✓ **Phase Transformation mechanism was revealed**

- Mn-migration to the Li-layer, occurring at high charge (instantaneous at x<0.5, sluggish at 0.5<x<1), is a key factor resulting the phase transformation to spinel-like structures
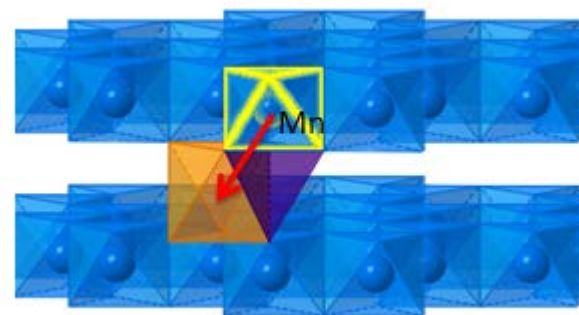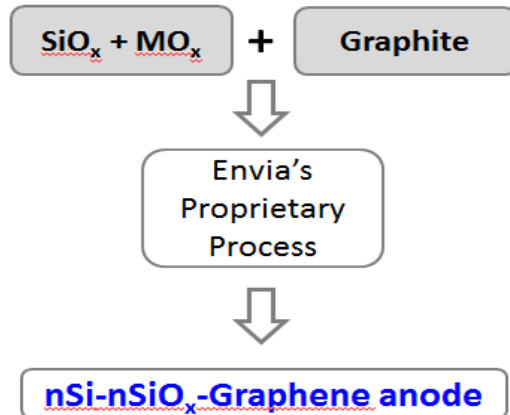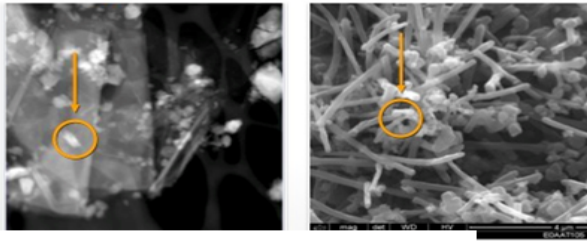

❑ **How to prevent it?**

In BATT program, effect of doping on the voltage fade has been explored. In the ABR project we are looking at stabilizing the structure via doping to eliminate the DC-R growth with respect to cycling

- Partially dope for Li to decrease the tendency for Mn migration
- Partially dope for Mn and increase the Mn-migration barriers

Source: LBNL

Si-C Anode Development

SiO$_x$ + MO$_x$ + Graphite → Envia's Proprietary Process → **nSi-nSiO$_x$-Graphene anode**

TEM/SEM analysis of Si-SiO$_x$-graphite anodes:

- Envia has developed an anode powder synthesis process using low cost precursors like SiO$_x$ and graphite

- Composition is proprietary (Si-SiO$_x$-Graphene) and patents have been filed

- Process is cheap, scalable and available in kg quantities
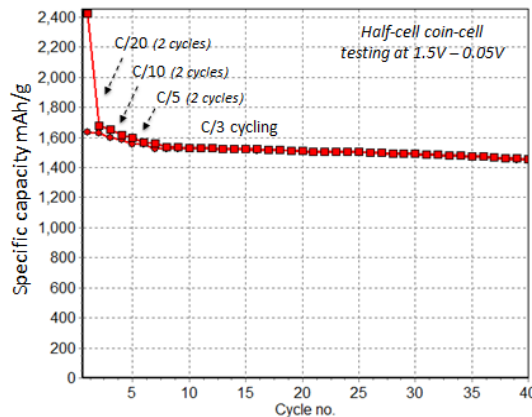
Embedded SiO$_x$ and Si particles between graphene sheets enhances mechanical stability and resistance against pulverization due to the large Si volume expansion explaining the improved cycle life
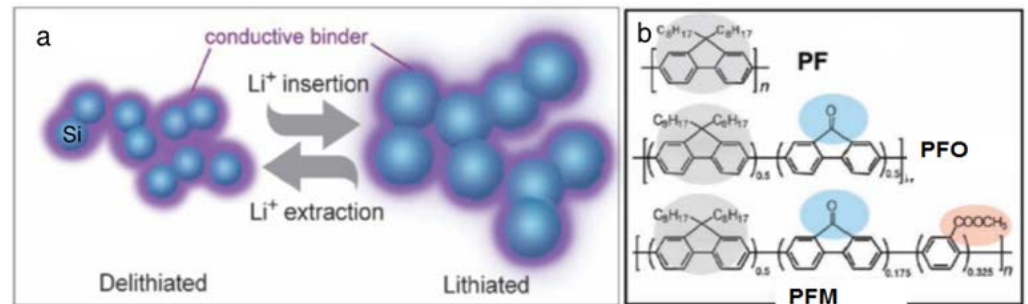
Envia's anode material will be paired with LBNL's conductive binder to enable long cycle and calendar life meeting ABR PHEV goals

Source: LBNL

ABR Baseline Cell

Data for 2 cells shown

Cell Chemistry:
HCMR™ Cathode and Si-SiO-C anode
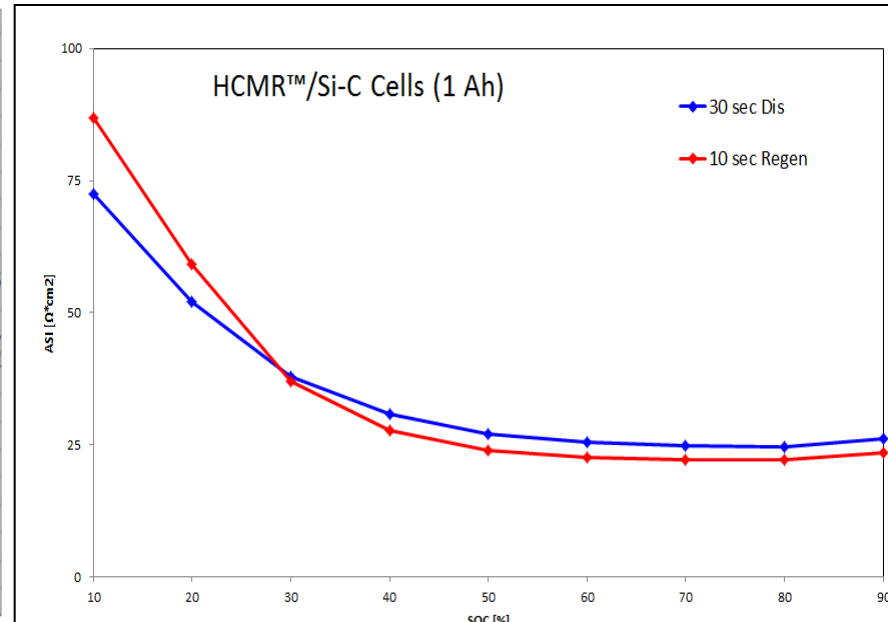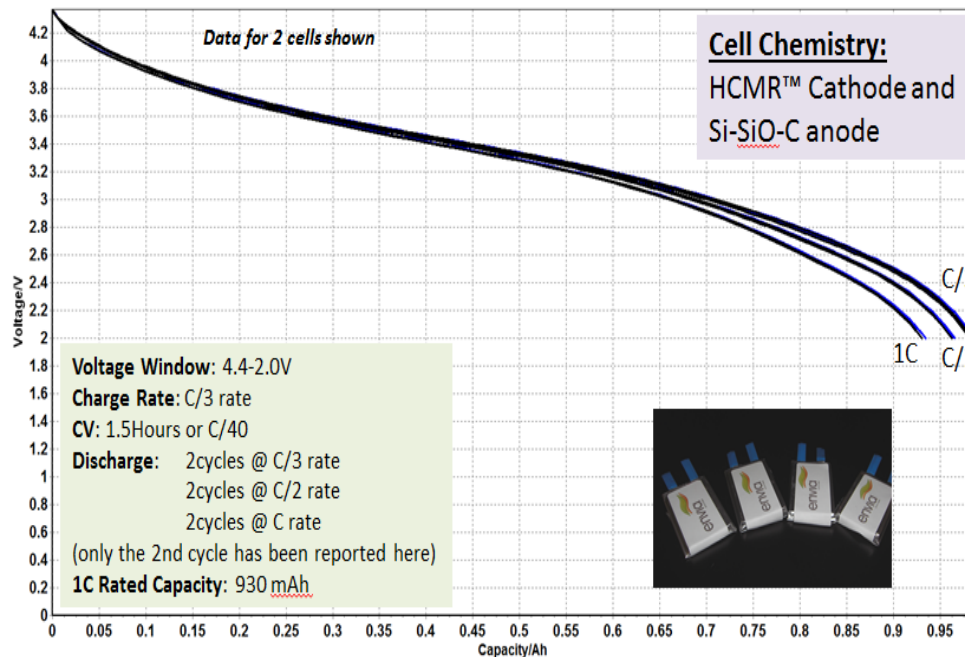
Voltage Window: 4.4-2.0V
Charge Rate: C/3 rate
CV: 1.5Hours or C/40
Discharge: 2cycles @ C/3 rate
        2cycles @ C/2 rate
        2cycles @ C rate
(only the 2nd cycle has been reported here)
1C Rated Capacity: 930 mAh

HCMR™/Si-C Cells (1 Ah)
— 30 sec Dis
— 10 sec Regen

- 930mAh capacity ABR baseline cells have been assembled and electrochemical performance (capacity & HPPC) is being tested and validated
- 12 ABR baseline cells were shipped to INL in April 2014 and testing protocols have been finalized
- DC-R measurements for the HCMR™/Si-C baseline cells show similar on-set as the Graphite cells
- Energy and power density evaluations, as well as, cycle life and calendar life are underway

Summary and Future Work

Summary:

- Conducting carbon coatings on cathode have reduced the DC-Resistance

- LiPON coatings on cathode have improved average voltage without compromising specific capacity

- ALD coatings on cathode have improved capacity retention, absolute average voltage and average voltage retention

- Phase transition mechanisms have been revealed by Atomistic modeling suggesting Mn migration to the Li layer

Future Work:

- Understand the root cause of DC-R and DC-R growth in HCMR™ cathodes using atomistic modeling and diagnostic tools

- Develop a cathode with low DC-R by optimizing the composition, dopants, nanocoating and synthesis conditions

- For LiPON coated HCMR™ materials (i) structural investigations using neutron diffraction & aberration corrected electron microscopy and (ii) metal ion dissolution and oxygen loss will be studied

- Taylor unique conducting binders to improve the cycle life of Si-C based anodes

- Optimize the integration of HCMR™ cathodes and Si-C anodes in a PHEV cell

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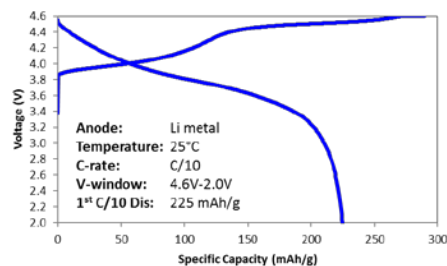- Jagjit Nanda
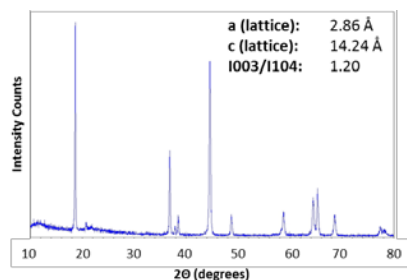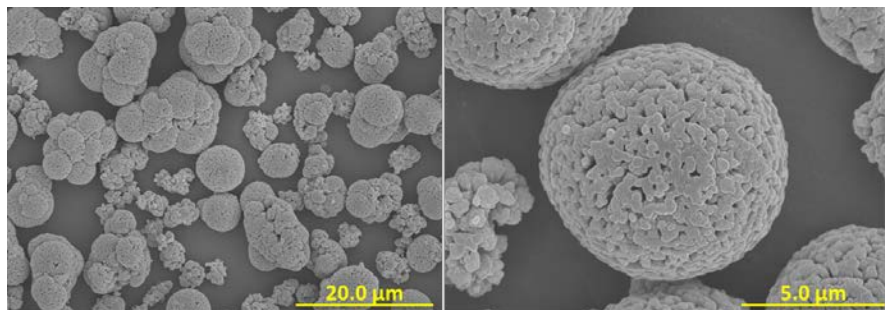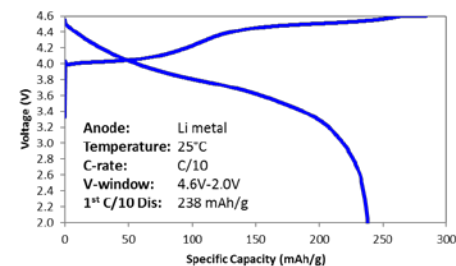- Nancy Dudney
- Gabrielle Veith

Technical Back up Slides

Baseline HCMR™-XLE Cathode Materials

HCMR^{TM} – XLE #1 (Uncoated)

a (lattice):	2.86 Å
c (lattice):	14.24 Å
I003/I104:	1.20

Anode: Li metal
Temperature: 25°C
C-rate: C/10
V-window: 4.6V-2.0V
1st C/10 Dis: 225 mAh/g

Measurement	Value
Primary Particle (nm)	201±26
D50 (µm)	8.44
FWHM (µm)	8.18
BET (m^2/g)	1.44
Tap Density (g/cc)	1.68
pH (Powder)	10.74
1st C/10 Charge (mAh/g)	289
1st C/10 Discharge (mAh/g)	225
Average Voltage at C/10 (V)	3.73

HCMR^{TM} – XLE #2 (Envia Nanocoated)

a (lattice):	2.86 Å
c (lattice):	14.25 Å
I003/I104:	1.60

Anode: Li metal
Temperature: 25°C
C-rate: C/10
V-window: 4.6V-2.0V
1st C/10 Dis: 238 mAh/g
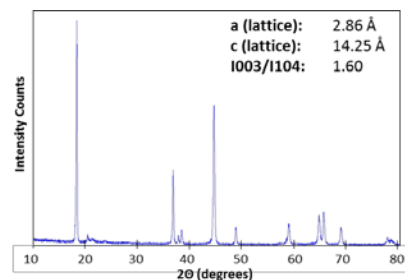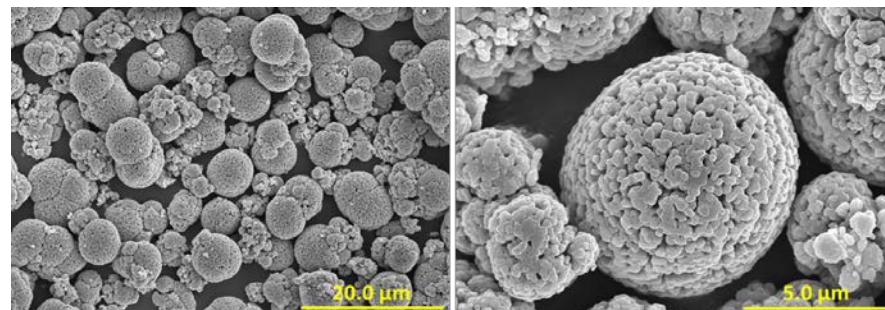
Measurement	Value
Primary Particle (nm)	217±17
D50 (µm)	8.27
FWHM (µm)	8.11
BET (m^2/g)	2.60
Tap Density (g/cc)	1.65
pH (Powder)	10.80
1st C/10 Charge (mAh/g)	284
1st C/10 Discharge (mAh/g)	238
Average Voltage at C/10 (V)	3.69

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SYSTEMS

HCMR™ XP vs. XLE - dQ/dV Analysis

HCMR™-XLE cathode
material shows Mn activity
upon repeated cycling
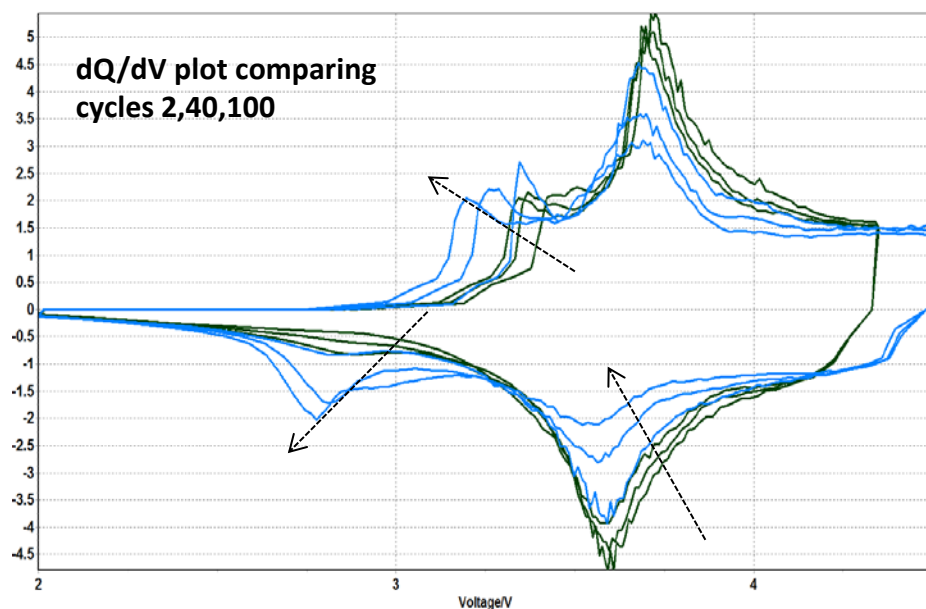
HCMR-XP cathode material
showing no Mn activity with
cycling
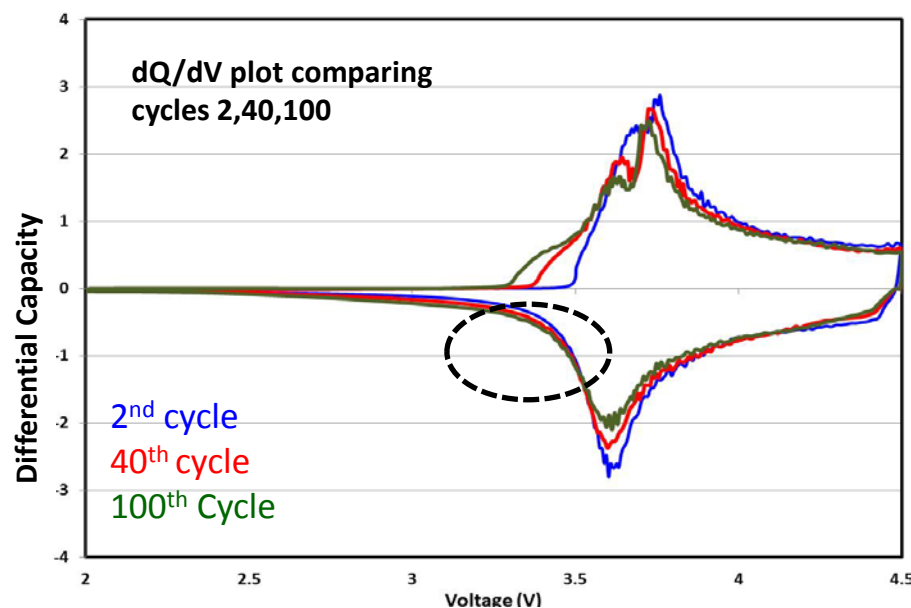
Data from full cell: HCMR™-XP/XLE vs Graphite

DCR Measurement Protocol

$$ASI = Area \frac{(Vrest - Vpulse)}{(Irest - Ipulse)}$$